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Samarium(III) compounds supported by the hydrotris(3,5-dimethyl-pyrazolyl)borate ligand: synthetic utility of the putative, reduction prone Sm(III)-hydrocarbyls, '$(Tp^{Me_2})_2SmR$'

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Dedicated with affection to Professor Alberto Romão Dias on the occasion of his 60th birthday

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Abstract

Addition of a stoichiometric amount of KR ($R = CH_2C_6H_4$-*o*-NMe_2, C_6H_4-o-CH_2NMe_2, $CH_2C_6H_5$) to a solution of $Sm(Tp^{Me_2})_2Cl$ in toluene or THF led to the immediate formation of the insoluble, purple $Sm(Tp^{Me_2})_2$ compound. However, when these reactions are carried out in the presence of protic substrates such as HOPh, HCp, HCCPh, HOC_6H_2-2,4,6-$^tBu_3$, $HNPh_2$ and 3,5-Me_2pzH, the corresponding $Sm(Tp^{Me_2})_2(Y)$ compounds (Y = OPh (**1**), CCPh (**2**), Cp (**3**), OC_6H_2-2,4,6-$^tBu_3$ (**4**), NPh_2 (**5**), 3,5-Me_2pz (**6**)) readily form and in good yields. The structures of **4**–**6** have been established by X-ray crystallography.

Keywords: Samarium complexes; Hydrotris(pyrazolyl)borate ligands; Crystal structures

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1. Introduction

The exploration of the molecular chemistry of organolanthanides and the spectacular advances made in this area owe much to the pentamethylcyclopentadienyl ligand [1,2]. However, in the past few years there has been increased interest in other alternative ligand systems [3].

We have focussed our attention on the study of hydrotris(pyrazolyl)borate anchored lanthanide compounds, in particular, on the reaction chemistry of $Sm(Tp^{Me_2})_2$ [4]. This compound undergoes facile one-electron transfer reactions leading to $Sm(Tp^{Me_2})_2X$ compounds where X is the mono-anionic form of O_2, PhNNPh, $OCPh_2$ and quinones [5]. However, the compound fails to react with protic substrates such as alcohols, amines, CpH or terminal alkynes. The known alkoxide derivatives, $Sm(Tp^{Me_2})_2OR$ (R = Ph, Ph–4-^tBu, C_5H_5N) [6,7], were obtained by salt metathesis of $Sm(Tp^{Me_2})_2Cl$ with NaOR, whereas $Sm(Tp^{Me_2})_2(CCPh)$ and $Sm(Tp^{Me_2})_2(Cp)$ are available by reacting $Sm(Tp^{Me_2})_2$ with $Hg(CCPh)_2$ [8] or TlCp [9], respectively. The hydrocarbyl derivatives $Sm(Tp^{Me_2})_2R$ are not known.

Here we describe our attempts to obtain $Sm(Tp^{Me_2})_2R$ compounds by metathesis of $Sm(Tp^{Me_2})_2$-Cl with the potassium salts of several hydrocarbyls. Although the compounds proved to be unstable, decomposing spontaneously to the reduced $Sm(Tp^{Me_2})_2$ species, we present circumstantial evidence to show that they have lifetime long enough to undergo protonolysis with several protic substrates. This procedure allows the preparation of the previously reported $Sm(Tp^{Me_2})_2$-(OPh) (**1**) [6], $Sm(Tp^{Me_2})_2(CCPh)$ (**2**) [8], and Sm-$(Tp^{Me_2})_2(Cp)$ (**3**) [9] compounds, and of the new complexes $Sm(Tp^{Me_2})_2Y$ (Y = OC_6H_2–2,4,6-$^tBu_3$ (**4**), NPh_2 (**5**), 3,5-Me_2pz (**6**)).

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2. Results and discussion

2.1. Reaction of $Sm(Tp^{Me_2})_2$ with KR reagents: reduction to $Sm(Tp^{Me_2})_2$

Addition of one equivalent of KR (R = $CH_2C_6H_4$-*o*-NMe_2, C_6H_4-*o*-CH_2NMe_2, $CH_2C_6H_5$) to a solution of $Sm(Tp^{Me_2})_2Cl$ in toluene or THF led to immediate formation of a purple precipitate and a pale purple solution. The precipitate is a mixture of the insoluble, purple, $Sm(Tp^{Me_2})_2$ compound and KCl. The solution, after simple work-up, revealed the presence of a small amount of $Sm(Tp^{Me_2})_2$ and unidentified organic products, Eq. (1):

$$Sm(Tp^{Me_2})_2Cl \xrightarrow[\text{toluene or THF}]{KR} Sm(Tp^{Me_2})_{2(s)} + KCl_{(s)} + \text{unidentified organic products} \quad (1)$$

No reaction was observed when KMe was added to a toluene solution of $Sm(Tp^{Me_2})_2Cl$. Stirring the mixture for more than 24 h ultimately led to decomposition.

A plausible explanation for the facile reduction of $Sm(Tp^{Me_2})_2Cl$, with concomitant formation of $Sm(Tp^{Me_2})_2$ and KCl, is homolytic cleavage of the Sm–C bond of the putative $Sm(Tp^{Me_2})_2R$ compounds. Although early reports on reduction of lanthanide(III) organometallics by alkali metal hydrocarbyls were restricted to Yb and Eu compounds [10,11], recently Gambarotta reported homolytic cleavage of a Sm–C bond of a Sm(III)–vinyl derivative supported by a calix-tetrapyrrole ligand [12]. The ease of decomposition of '$Sm(Tp^{Me_2})_2R$' is perhaps not surprising in view of the anticipated congested nature of the complexes and the attendant long and weak Sm(III)–R bond. Indeed, during our investigations on $Sm(Tp^{Me_2})_2$ we observed that the compound reacts preferentially with flat or narrow, cylindrical ligands which can fit into the cleft created by the '$Sm(Tp^{Me_2})_2$ fragment of the so obtained $Sm(Tp^{Me_2})_2Y$ compounds.

The instability of the putative '$Sm(Tp^{Me_2})_2R$' compounds led us to explore alternative means to ascertain, albeit indirectly, their existence. Protonolysis of the presumed Sm(III)–R bond offered one such possibility.

2.2. Reaction of $Sm(Tp^{Me_2})_2$ with KR in the presence of protic reagents: synthesis and characterization of $Sm(Tp^{Me_2})_2Y$ compounds

Slow addition of an equiv of $KC_6H_4CH_2NMe_2$ in toluene to stoichiometric amounts of $Sm(Tp^{Me_2})_2Cl$ and HOPh in the same solvent led, after stirring for 2 h, to a turbid solution. The KCl precipitate was filtered off and the solvent removed under reduced pressure. The remaining white solid was washed with *n*-hexane to remove the organic products. Compound **1**, $Sm(Tp^{Me_2})_2(OPh)$, was obtained in almost quantitative yield (Eq. (2)):

$$Sm(Tp^{Me_2})_2Cl + HOPh \xrightarrow[KR]{\text{toluene}} \underset{\mathbf{1}}{Sm(Tp^{Me_2})_2(OPh)} + KCl + RH \quad (2)$$

The $C_6H_5CH_2NMe_2$ by-product could be identified by recording the ^1H-NMR spectrum of the obtained solid prior to washing with *n*-hexane.

The same procedure was used for the synthesis of known $Sm(Tp^{Me_2})_2(CCPh)$ (**2**) and $Sm(Tp^{Me_2})_2(Cp)$ (**3**) and for the new compounds $Sm(Tp^{Me_2})_2(OC_6H_2-2,4,6\text{-}^tBu_3)$ (**4**), $Sm(Tp^{Me_2})_2(NPh_2)$ (**5**), and $Sm(Tp^{Me_2})_2(3,5\text{-}Me_2pz)$ (**6**). When the reactions were conducted in THF excess of the protic substrates had to be used for the preparation of **2**, **3**, **5** and **6**, otherwise the reactions did not go to completion and appreciable amounts of $Sm(Tp^{Me_2})_2Cl$ remained in the reaction mixture. In the case of $Sm(Tp^{Me_2})_2(Cp)$ (**3**), reduction was also observed in the absence of excess CpH both in toluene and THF.

Admittedly, the reactions outlined above could proceed via initial deprotonation of the protic substrates HY by KR, resulting in the formation of KY, followed by metathesis with $Sm(Tp^{Me_2})_2Cl$. Indeed $Sm(Tp^{Me_2})_2Cl$ undergoes metathesis with a variety of anionic reagents [6,7] and we have verified that it reacts with $K(OC_6H_2\text{–}2,4,6\text{-}^tBu_3)$, $KNPh_2$ and $K(3,5\text{-}Me_2pz)$ to give compounds **4**–**6**, respectively. However, the following observations indicate that the former reactions involve protonolysis of a transient Sm–C bond, at least in parallel with the deprotonation/metathesis pathway. Thus, although $Sm(Tp^{Me_2})_2Cl$ reacts with KCp or NaCp in toluene to give $Sm(Tp^{Me_2})_2(Cp)$ (**3**), the reaction in THF leads to substantial amounts of $SmCp_3 \cdot THF$ [13]. Formation of the latter is not observed when a mixture of $Sm(Tp^{Me_2})_2Cl$ and CpH is treated with KR in THF. In addition we have observed that whereas deprotonation of $HNPh_2$ by KR in toluene is slow, formation of **5** when KR is added to $Sm(Tp^{Me_2})_2Cl$ and $HNPh_2$ in the same solvent is rapid. Finally, the yields of compounds **4**–**6** are substantially higher by the 'KR to mixture of $Sm(Tp^{Me_2})_2Cl$/HY' protocol than by metathesis with preformed KY.

The $Sm(Tp^{Me_2})_2(Y)$ compounds are soluble in aromatic and ether type solvents, but are poorly soluble in aliphatic hydrocarbons, except for **4** which is moderately soluble in *n*-hexane.

Compounds **1**–**3** were identified by comparison of their ^1H-NMR spectra with those reported in the literature.

The IR spectra of **4**–**6** showed the typical ν(B–H) stretching vibration at about 2500 cm^{-1}, characteristic of a κ^3-coordination mode of the Tp^{Me_2} ligands [14].

The room temperature ^1H-NMR spectra of **4** and **5** exhibited six Tp^{Me_2} methyls and three 4-H singlets, consistent with C_2-symmetric structures for both compounds. In addition the spectra displayed resonances associated with the aryloxide and diphenylamide protons with the expected intensities and multiplicities.

The room temperature ^{1}H-NMR spectrum of **6** exhibited three broad resonances in a 3:3:1 ratio assigned to the Tp^{Me_2} ligands, with the resonance due to the 3-Me protons almost collapsed into the baseline. Two resonances with an intensity ratio 1:6 were assigned to proton H-4 and methyl protons of the 3,5-dimethylpyrazolide ligand. Cooling the toluene-d_8 solution resulted in progressive broadening and shifting of the proton resonances associated with the pyrazolylborate ligands. The low temperature limiting spectrum of **6** was obtained at − 50°C and is consistent with a C_2-symmetric structure.

3. Solid state structures

3.1. *Sm(Tp^{Me_2})$_2$(OC$_6$H$_2$—2,4,6-^{t}Bu$_3$)* (**4**)

The aryloxide **4** crystallized from *n*-hexane in the space group $P2_1/a$ with a molecule of solvent in the lattice. The molecular structure is shown in Fig. 1 and selected bond lengths and bond angles are given in Table 1. The solid-state structure consists of well-separated monomeric units with no significant intermolecular contacts. The metal centre is seven-coordinate by way of two tridentate pyrazolylborates and the aryloxide ligand. The coordination geometry is best described as distorted pentagonal bipyramidal with N(3) and N(5) occupying the apical sites, the N(3)–Sm–N(5) angle is 146.1(2)°. Although the solid-state structure has only C_1 symmetry, small angle deformations coupled with oscillation of the aryloxide ligand between pyrazolyl groups N(1) and N(4) are all that is necessary to result in a time-averaged C_2 molecular symmetry as found in solution.

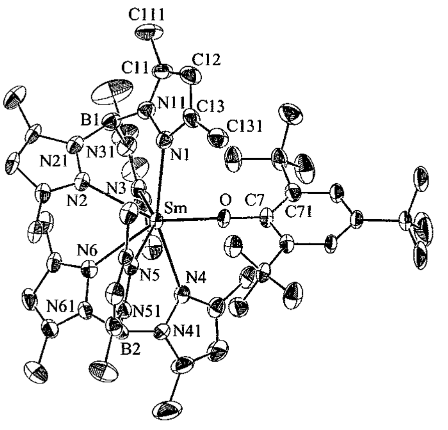

Fig. 1. ORTEP diagram of [Sm(Tp^{Me_2})$_2$(OC$_6$H$_2$ − 2,4,6-^{t}Bu$_3$)]·C$_6$H$_{14}$ using 35% probability ellipsoids.

Table 1
Selected bond lengths (Å) and bond angles (°) for **4**·C$_6$H$_{14}$, **5**·C$_7$H$_8$ and **6**

	4·C$_6$H$_{14}$	**5**·C$_7$H$_8$	**6**
Bond lengths			
Av. (Sm–N)$_{Tp}$	2.61(12)	2.56(7)	2.59(7)
Range (Sm–N)$_{Tp}$	2.468(6) -2.772(6)	2.478(7) -2.627(8)	2.486(5) -2.687(5)
Sm–O	2.188(5)		
Sm–N		2.435(11)	2.386(5), 2.363(5)
Bond angles			
B–Sm–B	136.6(2)	152.0(4)	146.0(2)
Sm–O–C	173.2(5)		
N(7)–Sm–N(8)			33.3(2)

The two Tp^{Me_2} ligands are bent back from each other at an angle of 136.6(2)°. This value is lower than the B–Sm–B angles found in previously reported Sm(Tp^{Me_2})$_2$X compounds and is understandable on the basis of the steric demands of the aryloxide ligand. This is also reflected in a longer Sm–O(1) bond length (2.188(5) Å) than the corresponding distance in Sm(Tp^{Me_2})$_2$(OPh − 4-^{t}Bu) (2.159(2) Å) [6], but compares with those in Sm(Tp^{Me_2})$_2$(OCPh$_2$) and Sm(Tp^{Me_2})$_2$(OC$_{13}$H$_8$) [5c] (2.201(3) and 2.186(4) Å, respectively). The geometrical requirements of the Tp^{Me_2} ligands also result in a longer Sm–O(1) bond length in comparison with the corresponding distance of 2.13(1) Å in the metallocene derivative (C$_5$Me$_5$)$_2$Sm(OC$_6$H–2,3,5,6-Me$_4$) [15].

Accordingly, the average Sm–N(pz) bond length of 2.61(12) Å (range 2.772−2.468 Å) is longer than the corresponding distance in the seven-coordinate Sm(Tp^{Me_2})$_2$(OPh − 4-^{t}Bu) [6] (2.572(5) Å), being only comparable with those in the eight-coordinate Sm(Tp^{Me_2})$_2$(OC$_5$H$_4$N) [7] (2.60(7) Å). The axial Sm–N(3) (2.488(6) Å) and Sm–N(5) (2.468(6) Å) bond lengths are shorter than those in the equatorial girdle (average 2.673(7) Å).

The boron atoms are tetrahedral and the twisting of the pyrazolyl groups are not exceptional (range 8−21°), although a higher distortion of the pyrazolyl rings closer to the large aryloxide ligand might have been anticipated.

3.2. *Sm(Tp^{Me_2})$_2$(NPh$_2$)* (**5**)

The diphenylamide complex **5** crystallized from toluene in the space group $C2/c$ with a molecule of toluene in the lattice. The molecular structure of **5** is shown in Fig. 2.

Selected bond lengths and angles are given in Table 1. The molecule has a crystallographic imposed twofold rotation axis, passing through the Sm and N(4) atoms. The geometry around the Sm centre may be regarded as pentagonal bipyramidal, with N(2) and N(2′) occupying the axial sites, the N(2)–Sm–N(2′) angle is 151.7(4)°. This symmetry is retained in solution as was inferred from the ^{1}H-NMR spectrum.

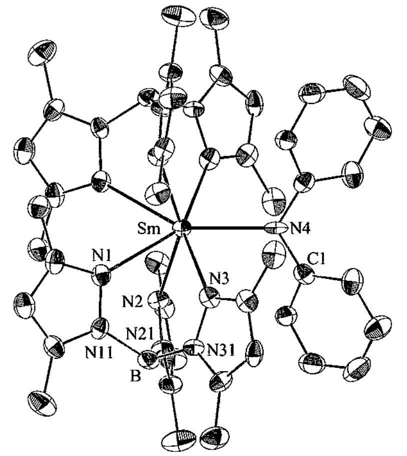

Fig. 2. ORTEP diagram of [Sm(Tp^{Me_2})$_2$(NPh$_2$)]·C_7H_8 using 35% probability ellipsoids.

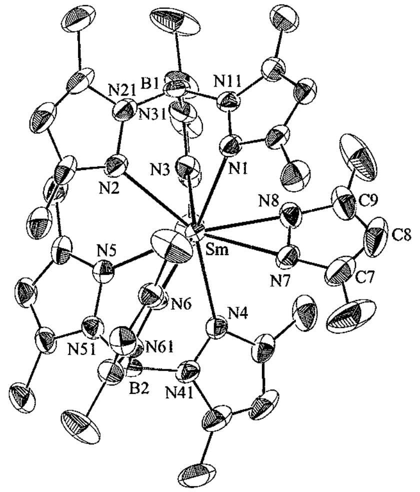

Fig. 3. ORTEP diagram of and [Sm(Tp^{Me_2})$_2$(3,5-Me$_2$pz)] using 30% probability ellipsoids.

The two Tp^{Me_2} ligands are bent back from each other at an angle of 152.0(4)°. The average Sm–N(pz) distance of 2.56(7) Å (range 2.627–2.478 Å) is shorter than that of **4** but compares with those in other seven-coordinate Sm(Tp^{Me_2})$_2$X compounds [5c,5d,6]. The Sm–N(4) distance (2.435(11) Å) is longer than the corresponding distance in the eight-coordinate Sm(Tp^{Me_2})$_2$(η^2-N$_2$Ph$_2$) [4] (2.386(8) and 2.418(8) Å) and in amido derivatives of the metallocenes Sm(C$_5$Me$_5$)$_2$[N(SiMe$_3$)$_2$] [16] (2.301(3) Å), Sm(C$_5$Me$_5$)$_2$(NHPh)(THF) [17] (2.331(3) Å), Sm(C$_5$Me$_5$)$_2$(η^2-PhNH*N*Ph)(THF) [17] (2.330(5) Å), and [Na(THF)$_2$(μ-η^5:η^5-MeC$_5$H$_4$)$_2$Sm(NPh$_2$)$_2$]$_n$ [18] (2.376(3) Å) but much shorter than the Sm(III)–N dative bonds in Sm(C$_5$Me$_5$)$_2$(N-MeIm)$_2$ (2.618(10) and 2.673(11) Å) [19] and in Sm(C$_5$Me$_5$)$_2$(η^2-Ph*N*HNPh)(THF) (2.610(5) Å) [17].

3.3. *Sm(Tp^{Me_2})$_2$(3,5-Me$_2$pz)* (**6**)

Crystals of the dimethylpyrazolide complex **6** were obtained by slow sublimation in vacuum at 210°C. The molecular structure is shown in Fig. 3 and selected bond lengths and angles are given in Table 1. The Sm atom is eight-coordinate being bonded to the six nitrogen atoms of the two tridentate Tp^{Me_2} ligands and to the two nitrogen atoms of the dimethylpyrazolide ligand. The coordination geometry can be described as dodecahedral. Alternatively, due to the small bite of the dimethylpyrazolide ligand (0.57 Å), the mid-point of the N–N bond of the pyrazolide group can be considered as occupying the seventh coordination site of a pentagonal bipyramid, with N(3) and N(6) in the axial positions (N(3)–Sm–N(6) equals 153.7(2)°) and the equatorial plane being defined by N(1), N(2), N(5), N(4) and the mean position between N(7) and N(8).

The two Tp^{Me_2} ligands are bent back from each other at an angle of 146.0(2)° being intermediate between **4** and **5**. The average Sm–N(pz) bond length is 2.59(7) Å (range 2.687–2.486 Å), also in between **4** and **5**, and in the range found for the corresponding distance in other seven-coordinate Sm(Tp^{Me_2})$_2$X compounds [5c,5d,6]. The Sm–N(7) (2.386(5) Å) and Sm–N(8) (2.363(5) Å) bond lengths are similar to the corresponding distances in the eight-coordinate [Yb(Ph$_2$Pz)$_2$(DME)$_2$] (2.424(7) Å) [20], after correction for the difference in the ionic radii of Yb(II) (1.14 Å) and Sm(III) (1.079 Å) [21].

In accord with the congested nature of the complex, the pyrazolyl rings N1N11 and N4N41 (those next to the pyrazolide ligand) are considerably twisted about their B–N bonds, with B–N–N–Sm torsion angles of 51(1) and 31(1)°, respectively.

4. Experimental

4.1. General procedures

All operations were performed using standard Schlenk line and dry box techniques under an inert atmosphere of nitrogen. THF, toluene, and *n*-hexane were dried by standard methods and degassed prior to use. Deuterated solvents, benzene-d_6 and toluene-d_8, were dried over Na and distilled. Sm(Tp^{Me_2})$_2$ [4] and Sm(Tp^{Me_2})$_2$Cl [22] were synthesized by reported methods. LiCH$_2$C$_6$H$_4$NMe$_2$ [23], LiC$_6$H$_4$CH$_2$NMe$_2$ [23] and LiCH$_2$C$_6$H$_5$ [24] were prepared as previously reported and converted into their potassium salts as described before [25]. The protic reagents, HOPh, HOC$_6$H$_2$–2,4,6-^{t}Bu$_3$, HNPh$_2$ and 3,5-Me$_2$pzH were sublimed prior to use and the corresponding potassium salts were obtained by reacting a stoichiometric amount of KH with the appropriate reagent in THF. ^{1}H-NMR spectra were recorded on Varian VXR 300 spectrometer and referenced internally using the residual solvent resonances relative to $\mathrm{Me_4Si}$. IR spectra were recorded on a Perkin–Elmer 2000 FT-IR spectrometer. Carbon, hydrogen and nitrogen analyses were performed in-house using a Perkin–Elmer automatic analyser.

4.2. Synthetic procedures

4.2.1. $\mathrm{Sm(Tp^{Me_2})_2(OPh)}$ (**1**)

To a solution of $\mathrm{Sm(Tp^{Me_2})_2Cl}$ (110 mg, 0.14 mmol) and HOPh (14 mg, 0.14 mmol) in toluene was slowly added 24 mg (0.14 mmol) of $\mathrm{KC_6H_4CH_2NMe_2}$ in the same solvent. After stirring for 2 h the precipitate of KCl was filtered off and the solvent was removed under vacuum. The white solid was washed with *n*-hexane and vacuum dried.

^{1}H-NMR (benzene-d_6, 25°C, δ ppm): 11.20 (2H, d, H_o); 8.32 (2H, t, H_m); 7.81 (1H, t, H_p); 5.39 (6H, s, 4-H); 3.09 (18H, s, $\mathrm{C}H_3$(5)); −1.74 (18H, s, $\mathrm{C}H_3$(3)).

4.2.2. $\mathrm{Sm(Tp^{Me_2})_2(CCPh)}$ (**2**)

The compound was prepared as described for **1** by using 105 mg (0.13 mmol) of $\mathrm{Sm(Tp^{Me_2})_2Cl}$, excess of HCCPh (30 µl, 0.27 mmol) and 24 mg (0.13 mmol) of $\mathrm{KC_6H_4CH_2NMe_2}$.

^{1}H NMR (benzene-d_6, 25°C, δ ppm): 9.03 (2H, d, H_o); 7.65 (2H, t, H_m); 7.35 (1H, m, H_p); 5.45 (6H, s, 4-H); 2.93 (18H, s, $\mathrm{C}H_3$(5)); −1.10 (18H, br, $\mathrm{C}H_3$(3)).

4.2.3. $\mathrm{Sm(Tp^{Me_2})_2(Cp)}$ (**3**)

The preparation was carried out as described for **1** by adding a solution of $\mathrm{KCH_2C_6H_5}$ (15.2 mg, 0.12 mmol) in THF to a solution of $\mathrm{Sm(Tp^{Me_2})_2Cl}$ (91 mg, 0.13 mmol) in the same solvent, in the presence of excess of CpH (20 µl, 0.24 mmol).

^{1}H NMR (benzene-d_6, 20°C, δ ppm): 9.85 (5H, s, $\mathrm{C_5}H_5$); 6.52 (1H, s, 4-H); 6.10 (1H, s, 4-H); 5.33 (2H, s, 4-H); 4.80 (3H, s, $\mathrm{C}H_3$); 4.73 (2H, s, 4-H); 2.65 (6H, s, $\mathrm{C}H_3$); 2.48 (3H, s, $\mathrm{C}H_3$); 2.33 (3H, s, $\mathrm{C}H_3$); 2.21 (6H, s, $\mathrm{C}H_3$); 1.41 (3H, s, $\mathrm{C}H_3$); −0.44 (6H, s, $\mathrm{C}H_3$); −2.20 (6H, s, $\mathrm{C}H_3$).

4.2.4. $\mathrm{Sm(Tp^{Me_2})_2(OC_6H_2\text{–}2,4,6\text{-}^tBu_3)}$ (**4**)

(a): To a solution of $\mathrm{Sm(Tp^{Me_2})_2Cl}$ (202 mg, 0.26 mmol) and $\mathrm{HOC_6H_2\text{–}2,4,6\text{-}^tBu_3}$ (68 mg, 0.26 mmol) in THF was slowly added 131 mg (0.26 mmol) of $\mathrm{KCH_2Ph}$ in the same solvent. There is immediate formation of a yellow solution. After stirring overnight the KCl precipitate was filtered off and the solvent removed under vacuum. The resulting yellow residue was extracted with n-hexane and the volume of the extract reduced under vacuum. Yellow crystals of $\mathrm{Sm(Tp^{Me_2})_2(OC_6H_2 - 2,4,6\text{-}^tBu_3)}$ were obtained from this solution. Yield: 60% (150 mg, 0.15 mmol). Anal. Found: C, 57.32; H, 7.41; N, 16.30. Calc. for $\mathrm{C_{48}H_{73}N_{12}B_2SmO}$: C, 57.30; H, 7.31; N, 16.71%. IR (Nujol, cm^{-1}): 2510 (sh), 2550 (B–H). ^{1}H-NMR (benzene-d_6, 21°C, δ ppm): 8.66 (2H, s, H_m); 6.63 (2H, s, 4-H); 5.33 (2H, s, 4-H); 3.84 (2H, s, 4-H); 3.16 (6H, s, $\mathrm{C}H_3$); 3.14 (6H, s, $\mathrm{C}H_3$); 2.87 (6H, s, $\mathrm{C}H_3$); 2.83 (6H, s, $\mathrm{C}H_3$); 2.45 (18H, s, $\mathrm{C(C}H_3)_3$); 1.96 (9H, s, $\mathrm{C(C}H_3)_3$); 0.35 (6H, s, $\mathrm{C}H_3$); −8.70 (6H, s, $\mathrm{C}H_3$).

(b): Slow addition of a solution of $\mathrm{KOC_6H_2\text{-}2,4,6\text{-}^tBu_3}$(106 mg, 0.35 mmol) in THF to $\mathrm{Sm(Tp^{Me_2})_2Cl}$ (275 mg, 0.35 mmol) in the same solvent led to the formation of a pale-yellow solution from which **4** was isolated as described in (a) in moderate yield (35%, 0.12 mmol). Anal. Found: C, 56.02; H, 7.52; N, 16.08. Calc. for $\mathrm{C_{48}H_{73}N_{12}B_2SmO}$: C, 57.30; H, 7.31; N, 16.71%.

4.2.5. $\mathrm{Sm(Tp^{Me_2})_2(NPh_2)}$ (**5**)

(a): To a solution of $\mathrm{Sm(Tp^{Me_2})_2Cl}$ (108 mg, 0.14 mmol) and $\mathrm{HNPh_2}$ (23 mg, 0.14 mmol) in toluene was slowly added 24 mg (0.14 mmol) of $\mathrm{KC_6H_4CH_2NMe_2}$ in the same solvent. There is immediate formation of an orange-reddish solution. After stirring overnight, the precipitate of KCl was separated and the solvent was removed under vacuum. The orange solid was washed with *n*-hexane and vacuum dried. Yield: 80% (102 mg, 0.11 mmol). Anal. Found: C, 56.73; H, 6.01; N, 19.46. Calc. for $\mathrm{C_{42}H_{54}N_{13}B_2Sm}$: C, 55.26; H, 5.96; N, 19.94%. IR (Nujol, cm^{-1}): 2540 (B–H). ^{1}H-NMR (benzene-d_6, 25°C, δ ppm): 6.98 (2H, t, H_p); 6.81 (4H, t, H_m); 6.68 (2H, s, 4-H); 5.83 (4H, d, H_o); 5.33 (2H, s, 4-H); 3.87 (2H, s, 4-H); 3.66 (6H, s, $\mathrm{C}H_3$); 2.97 (6H, s, $\mathrm{C}H_3$); 2.24 (6H, s, $\mathrm{C}H_3$); 1.74 (6H, s, $\mathrm{C}H_3$); 1.33 (6H, s, $\mathrm{C}H_3$); −0.59 (6H, s, $\mathrm{C}H_3$).

(b): Solid $\mathrm{KNPh_2}$ (53mg, 0.26mmol) was added to a solution of $\mathrm{Sm(Tp^{Me_2})_2Cl}$ (200 mg, 0.26 mmol) in toluene, at room temperature (r.t.). There was immediate formation of a white precipitate and an orange-reddish solution. After stirring for 2 h, the precipitate of KCl was removed and the solution was evaporated to dryness. Crystallization of the residue from a concentrated toluene solution yielded the orange–red $\mathrm{Sm(Tp^{Me_2})_2(NPh_2)}$ compound in 65% yield (150 mg, 0.16 mmol). Anal. Found: C, 54.89; H, 6.08; N, 18.92. Calc. for $\mathrm{C_{42}H_{54}N_{13}B_2Sm}$: C, 55.26; H, 5.96; N, 19.94%.

4.2.6. $\mathrm{Sm(Tp^{Me_2})_2(3,5\text{-}Me_2pz)}$ (**6**)

(a): To a solution of $\mathrm{Sm(Tp^{Me_2})_2Cl}$ (100 mg, 0.13 mmol) and 3,5-$\mathrm{Me_2pzH}$ (12 mg, 0.13 mmol) in toluene was slowly added 22 mg (0.13 mmol) of $\mathrm{KC_6H_4CH_2NMe_2}$ in the same solvent. After stirring for 2 h, the precipitate was separated and the solvent was removed under reduced pressure. The resultant white residue was washed with hexane. Yield: 90% (100 mg, 0.12 mmol). Anal. Found: C, 49.62; H, 5.91; N, 20.94. Calc. for $\mathrm{C_{35}H_{51}N_{14}B_2Sm}$: C, 50.05; H, 6.12; N, 23.35%. IR (Nujol, cm^{-1}): 2540 (sh), 2500 (B–H). ^{1}H-NMR (toluene-d_8, 27°C, δ ppm): 7.89 (1H, s, 4-H(pz)); 5.37 (6H, br, 4-H); 4.04 (6H, s, $\mathrm{C}H_3$(pz)); 2.71 (18H, s, $\mathrm{C}H_3$(5)); −1.20 (18H, br, $\mathrm{C}H_3$(3)). ^{1}H-NMR (toluene-

d_8, -50°C, δ ppm): 8.74 (1H, s, 4-H(pz)); 6.56 (2H, s, 4-H); 5.37 (2H, s, 4-H); 4.96 (2H, s, 4-H); 4.24 (6H, s, CH_3(pz)); 3.95 (6H, s, CH_3), 3.20 (6H, s, CH_3), 2.89 (6H, s, CH_3), 2.83 (6H, s, CH_3), -0.72 (6H, s, CH_3), -8.37 (6H, s, CH_3).

(b): A solution of K(3,5-Me$_2$Pz) (51 mg, 0.38 mmol) in THF was added to a solution of Sm(Tp^{Me_2})$_2$Cl (296 mg, 0.38 mmol) in the same solvent. After stirring overnight the KCl was separated from the supernatant solution. Removal of the solvent under vacuum followed by extraction with CH$_2$Cl$_2$ gave the white compound, Sm(Tp^{Me_2})$_2$(3,5-Me$_2$pz) (**6**). Yield 47% (150 mg, 0.18 mmol). Anal. Found: C, 48.28; H, 6.23; N, 21.05. Calc. for $C_{35}H_{51}N_{14}B_2Sm$: C, 50.05; H, 6.12; N, 23.35%.

4.3. X-ray crystallographic analysis

Pale yellow crystals of **4** were grown from a concentrated solution of n-hexane. Crystals of **5** (orange-reddish) were grown from a concentrated solution of toluene. Vacuum sublimation at 210°C permitted the isolation of **6** as transparent plates. The crystals were mounted in thin-walled glass capillaries in a nitrogen-filled glove-box. Data were collected at r.t. on an Enraf–Nonius CAD4-diffractometer, with graphite-monochromated Mo–K$_\alpha$ radiation, using the ω–2θ scan technique. The data were corrected [26] for Lorentz and polarization effects, for linear decay and empirically for absorption by Ψ scans. Table 2 summarizes the crystallographic data. The structures were solved by Patterson methods [27] and developed by alternating cycles of full-matrix least-squares refinement on F^2 and difference Fourier techniques, using SHELXL-93 [28]. For compound **4** a disordered hexane molecule and for **5** a severely disordered toluene solvent molecule near a centre of symmetry were localized in the asymmetric unit. All the non-hydrogen atoms were refined with anisotropic thermal motion parameters, except the carbon atoms of the solvent in **4**. The contributions of the hydrogen atoms were included at calculated positions (except those of the solvent molecules). Atomic scattering factors and anomalous dispersion terms were taken from Ref. [28]. The illustrations were made with ORTEPII [29] and all calculations were performed on a Dec-alpha 3000 computer.

5. Conclusions

Attempts to isolate Sm(Tp^{Me_2})$_2$R type compounds have so far proven unsuccessful. The putative Sm(III)–R bond is unstable and undergoes spontaneous reduction to Sm(Tp^{Me_2})$_2$ and uncharacterized organic by-products. Neverthless, the protocol of treating mixtures of Sm(Tp^{Me_2})$_2$Cl/HY with KR is synthetically useful and provides Sm(Tp^{Me_2})$_2$Y compounds in good yields. Further studies, aimed at isolating and/or providing more conclusive evidences for the existence of Sm(Tp^{Me_2})$_2$R are underway.

Table 2
Crystal data and structure refinement parameters for complexes **4**·C_6H_{14}, **5**·C_7H_8 and **6**

	4·C_6H_{14}	**5**·C_7H_8	**6**
Empirical formula	$C_{48}H_{73}B_2N_{12}OSm\cdot C_6H_{14}$	$C_{42}H_{54}B_2N_{13}Sm\cdot C_7H_8$	$C_{35}H_{51}B_2N_{14}Sm$
Formula weight	1092.33	1005.09	839.87
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/a$	$C2/c$	$P2_1/c$
Unit cell dimensions			
a (Å)	18.697(3)	16.668(4)	10.646(1)
b (Å)	14.638(2)	16.996(3)	22.397(1)
c (Å)	21.496(2)	17.610(3)	17.167(1)
β (°)	96.986(11)	98.61(2)	95.884(7)
V (Å^3)	5839.5(13)	4933(2)	4071.7(5)
Z	4	4	4
D_{calc} (g cm^{-3})	1.242	1.353	1.370
μ (Mo–K$_\alpha$) (mm^{-1})	1.052	1.238	1.486
Theta range for data collection (°)	1.5–24.0	1.5–25.0	1.5–24.0
Reflections collected	9424	4470	5584
Observed [$I>2\sigma(I)$]	5779	2850	4101
Independent reflections (R_{int})	9153 (0.0499)	4313 (0.0451)	5277 (0.0515)
Parameters	601	308	469
R_1 [a]	0.0610	0.0763	0.0395
wR_2 [b]	0.1142	0.1418	0.0738
Goodness-of-fit on F^2	1.060	1.072	1.090

[a] $R_1=\Sigma||F_o|-|F_c||/\Sigma|F_o|$.

[b] $wR_2=[\Sigma(w(F_o^2-F_c^2)^2)/\Sigma(w(F_o^2)^2)]^{1/2}$; $w=1/[\sigma^2(F_o^2)+(aP)^2+bP]$, where $P=(F_o^2+2F_c^2)/3$.

6. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 158315, 158316 and 158317 for compounds **4**–**6**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: + 44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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